the sample, these behaviors are expected. Table I shows that the values are in reasonable agreement with those calculated by the standard procedures. Table II shows that the method can also be used for the estimation of tetraphenylborate with standard silver or thallium(I) nitrate.

Crane (*2*, *3*), in a study of the potentiometric titration of negative tetraphenylborate ion with silver nitrate, found that the results obtained using sodium chloride instead of potassium tetraphenylborate as a primary standard deviate by 5.4%. Kirsten *et al.* (*7*) attributed this discrepancy to the tendency of silver ion to precipitate more tetraphenylborate than that required for one valence. The standardization of silver nitrate against potassium tetraphenylborate under the conditions used in the determination was therefore recommended. However, Findeis and De Vries (*4*) performed experiments using the amperometric end point for the titration of the tetraphenylborate part of the potassium compound with silver nitrate and noticed no discrepancy. They reported accurate results for potassium on the basis of silver nitrate as a standard. Similarly, the argentometric titration of tetraphenylborate part using eosin (*10*) or chromate (*5*) indicator gave good results. The results reported here show that the precipitation of silver or thallium tetraphenylborate takes place stoichiometrically under the conditions described in a 1 to 1 ratio.

Although the high frequency method is not very accurate, its ability to accommodate small concentrations of materials in comparatively high dilutions is a distinct advantage.

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Composition of a Tetraalkylammonium Base Titrant

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▶ The strongly basic titrant prepared by reaction of tetra-*n*-butylammonium iodide with silver oxide in anhydrous methanol has been found to be a 1 to 1 mixture of hydroxide and methoxide. The concept of a mixed hydroxide-alcoholate base titrant should apply generally to titrants prepared by reaction of quaternary ammonium halides with silver oxide in anhydrous alcohols.

A MAJOR CONTRIBUTION to the technique of titrating weak acids in nonaqueous media was the introduction of practical means of preparing anhydrous tetraalkylammonium base titrants. The first successful methods for preparing such titrants were published simultaneously (*1*, *3*). The ion exchange method developed by Harlow *et al.* (*3*) produces a wholly hydroxide titrant. The titrant prepared by the Cundiff and Markunas method (*1*) has been described frequently in the literature as an hydroxide also. However, an attempt to write an equation for the reaction involved suggested that the actual composition is a mixture of hydroxide and methoxide. The method consists of treating a quaternary ammonium iodide dissolved in anhydrous methanol with excess silver oxide, filtering, and then diluting the methanolic solution of the resultant base 1 to 10 with dry benzene.

This paper reports the experimental verification of a mixed base titrant when the titrant is prepared by the Cundiff and Markunas method.

EXPERIMENTAL

Tetra-*n*-butylammonium iodide (containing no significant amount of water by Karl Fischer titration and at least 98% pure by iodide analysis) was dissolved in reagent grade methanol (0.05% water) and finely powdered silver oxide (100.0% by silver analysis) was added, in the relative amounts reported by Cundiff and Markunas (*1*). The glass-stoppered flask containing the reaction mixture was filled with dry, carbon dioxide–free nitrogen and was shaken vigorously on a mechanical shaker for 90 minutes. After the solids had settled, the clear supernatant was analyzed for hydroxide and total base content.

The total base content was determined by adding an aliquot of the supernatant directly to an excess of standard hydrochloric acid and back-titrating the excess with standard sodium hydroxide. The hydroxide content was determined by adding an aliquot of the supernatant to a methanol solution containing a fifteenfold excess of glacial acetic acid. The amount of water formed on neutralization was determined by Karl Fischer titration. Two experiments were run and the results are given below.

	Experiment	
	1	2
Total base content, meq./ml.[a]	0.85	0.97
Hydroxide content, meq./ml.	0.46	0.52

[a] Theoretical total base content was 1.0 meq./ml. Apparently reaction was not complete in experiment 1.

DISCUSSION

The data show that the total base titer of the methanolic solution was very nearly twice the hydroxide titer in each experiment. Thus, it appears that the base titrant prepared by reaction of a quaternary ammonium iodide dissolved in anhydrous methanol with silver oxide is a 1 to 1 mixture of hydroxide and methoxide. The hydroxide titer in excess of one half the total can be accounted for by the amount of water present in the methanol used as solvent. If sufficient water is present, it is expected that a wholly hydroxide titrant would be prepared.

The following equation is suggested for the reaction involved:

$$2R_4N^+I^- + Ag_2O + CH_3OH \xrightarrow[\text{solvent}]{CH_3OH} 2AgI + R_4N^+OH^- + R_4N^+OCH_3^-$$

No other equation appears to be applicable, particularly one which suggests the preparation of a wholly hydroxide titrant under essentially anhydrous conditions.

In preparations of the titrant by the writer, the methanolic solutions of the mixed base were diluted 1 to 10 with benzene containing 0.011% water. If all the water added in the dilution reacted with methoxide to give hydroxide, as seemed to be the case in the methanol solutions, at least 40% of the total base titer of the titrants was still methoxide. No adverse effects were observed when using the mixed base titrant for titrating very weak organic H acids. Normal titrations were obtained in acetone, acetonitrile, dimethylformamide, pyridine, *n*-butylamine, ethylenediamine, and piperidine.

Quaternary ammonium hydroxide titrants can be prepared by methods which preclude the formation of methoxide. Examples are the van der Heijde and Dahmen method (*4*), which involves reaction of aqueous suspensions of the iodide with silver oxide, and the Harlow *et al.* method (*3*), in which an alcoholic solution of the iodide is passed through a bed of anion exchange resin in the hydroxide form. In these titrant solutions there is probably a trace amount of methoxide in equilibrium with the hydroxide. However, this methoxide has an entirely different origin and is present in a considerably smaller amount relative to the hydroxide than the methoxide formed in the Cundiff and Markunas method.

Harlow and Bruss (*2*), in reporting the preparation of a quaternary ammonium base titrant by reaction of the iodide with silver oxide in isopropyl alcohol, state that the titrant is an equilibrium mixture of hydroxide and isopropylate. However, these investigators do not delineate any particular concept regarding the origin of the methoxide nor do they indicate its concentration relative to that of the hydroxide. Based on the work described in this paper one would immediately suggest, and possibly be correct in doing so, that the titrant is a 1 to 1 mixture of hydroxide and isopropylate. However, caution must be exercised in applying the concept of a mixed base titrant as described herein. This is because certain alcohols containing a dissolved quaternary ammonium iodide may not participate in reaction with silver oxide to form equal amounts of alcoholate and hydroxide. That a reaction takes place in a particular alcohol simply may mean that sufficient water is present and a wholly hydroxide titrant is formed. Either analysis to show that the reactants and solvent are anhydrous or analysis to determine the hydroxide titer *vs.* the total base titer of the prepared titrant is necessary to know the actual composition of a titrant prepared by the Cundiff and Markunas method.

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A Recording Titrator

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▶ A simple, rugged, compact, and highly accurate recording titrator (pH-stat) has been designed and constructed. Data are presented demonstrating its sensitivity, freedom from drift, accuracy, and ability to utilize small samples.

The potentiometric titration of acidic or basic groups liberated in the course of the reaction of hydrolytic enzymes has become a standard method in many laboratories. Although the techniques employed are varied, most of these depend upon commercial pH meters and may utilize equipment for recording the amount of reagent required to maintain a constant pH (*1*, *4*, *5*). A highly accurate recording titrator (pH-stat) was designed and constructed for studies in which the maximum economy in substrates and enzymes could be effected by the use of small samples and varied time periods for the experimental runs. The present paper describes this instrument and its performance.

DESCRIPTION OF APPARATUS

The completed instrument (Figure 1) consists of the potentiometer, the recorder which plots volume of reagent added against time of reaction, and a thermostated reaction vessel containing the electrode assembly.

Potentiometer. The measuring device was designed to conform to the following criteria:

It must not load the source, because glass electrodes have internal resistances of the order of 3 × 10^8 to 1 × 10^9 ohms.

Long-term drift must be negligible.

Response should be rapid.

It must be accurate.

It must be line-operated and immune to line voltage fluctuations.

The glass electrode potential is compared to a set potential by means of a mechanical switch modulator. Output from the modulator is fed into an electrometer tetrode, followed by four stages of voltage amplification and a power phase detector whose output is applied to one phase of a two-phase servo motor; this in turn drives the pipetting device and the recorder pen simultaneously. The circuit is shown in Figure 2.

The cover and base were removed from a Brown converter and the following modifications made: The screw which holds the stack together was removed, care being taken not to disturb the position of the elements. A polystyrene sleeve, with thicker walls, replaced the fiber insulating sleeve and a screw of smaller diameter was substituted for the one removed. The driver coil was removed and fitted with internal and external shields, so constructed that the reed was completely electrostatically